AQUA AMMONIA PROCESS FOR GREENHOUSE AND ACID GAS REMOVAL

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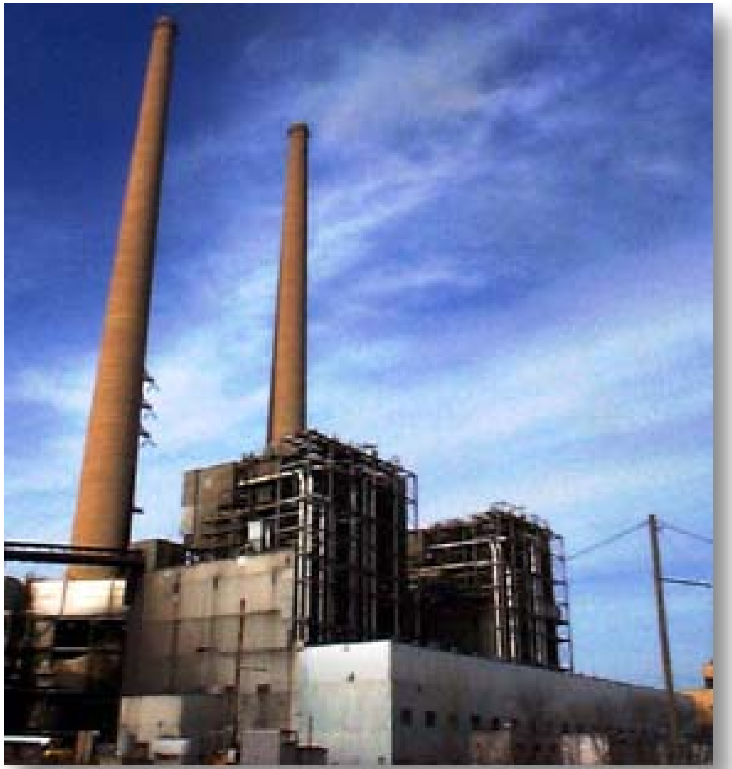
OVERVIEW

To develop a knowledge/data base to determine whether an ammonia scrubbing process is a viable regenerable-capture technique that can simultaneously remove carbon dioxide, sulfur dioxide, nitric oxides, and trace pollutants from flue gas.



FOSSIL ENERGY PROGRAM RELATIONSHIP

- **CARBON SEQUESTRATION**
  – The separation and capture area is aimed at developing technologies with low capital cost, low parasitic load, high percent reduction in emissions, and the capability to integrate with pollutant controls.

- **INNOVATIONS FOR EXISTING PLANTS**
  – The pursuit of multi-pollutant, multi-media solutions is desirable since integrated systems have lower costs due to fewer subsystems, lower parasitic losses and associated derating, and a smaller plant footprint.

PROJECT HISTORY

- Began in FY2002 as part of an international collaborative effort with China under Annex IV: Energy and Environmental Control Technologies of the New Fossil Energy Protocol.

- “Study of CO_2 Sequestration by Spraying Concentrated Aqueous Ammonia and Production of a Modified Ammonium Bicarbonate Fertilizer”

NETL

BACKGROUND: CO_2/NH_3

- Ammonia recovered in coke oven gas and used as absorbent for hydrogen sulfide.
- Some kinetic studies exist on ammonia/carbon dioxide systems (Pinsent et al. 1956) but little information in the temperature range of interest.
- China has produced ammonium bicarbonate as a fertilizer since the 1960s.
- Bai et al. (1997, 1999) investigated the reaction of CO_2 in aqueous ammonia as a possible sequestration capture reaction.

BACKGROUND: $SO_2/NO_x/NH_3$

- Commercial processes (Marsulex and Walther) exist for SO_2-ammonia scrubbing.
- Ammonia processes (high temperature) exist for NO_x removal (SCR).
- Combined SO_2/NO_x removal can be obtained in the presence of ammonia by using an e-beam (Ebara process, a dry process).
- NO_2 can react with aqueous ammonia (Shale et al., 1971).
- ECO process simultaneously controls SO_2, NO_x, and Hg by ammonia scrubbing.

AQUA AMMONIA PROCESS CHEMISTRY
(absorption)

- $2\ NH_3 + CO_2 \longrightarrow NH_2COONH_4$
- $NH_2COONH_4 + CO_2 + 2\ H_2O \longrightarrow 2\ NH_4HCO_3$
- $NH_2COONH_4 + H_2O \longrightarrow NH_4HCO_3 + NH_3$
- $NH_3 + H_2O + CO_2 \longrightarrow NH_4HCO_3$
- $2\ NH_3 + H_2O + CO_2 \longrightarrow (NH_4)_2CO_3$
- $(NH_4)_2CO_3 + CO_2 + H_2O \longrightarrow 2\ NH_4HCO_3$

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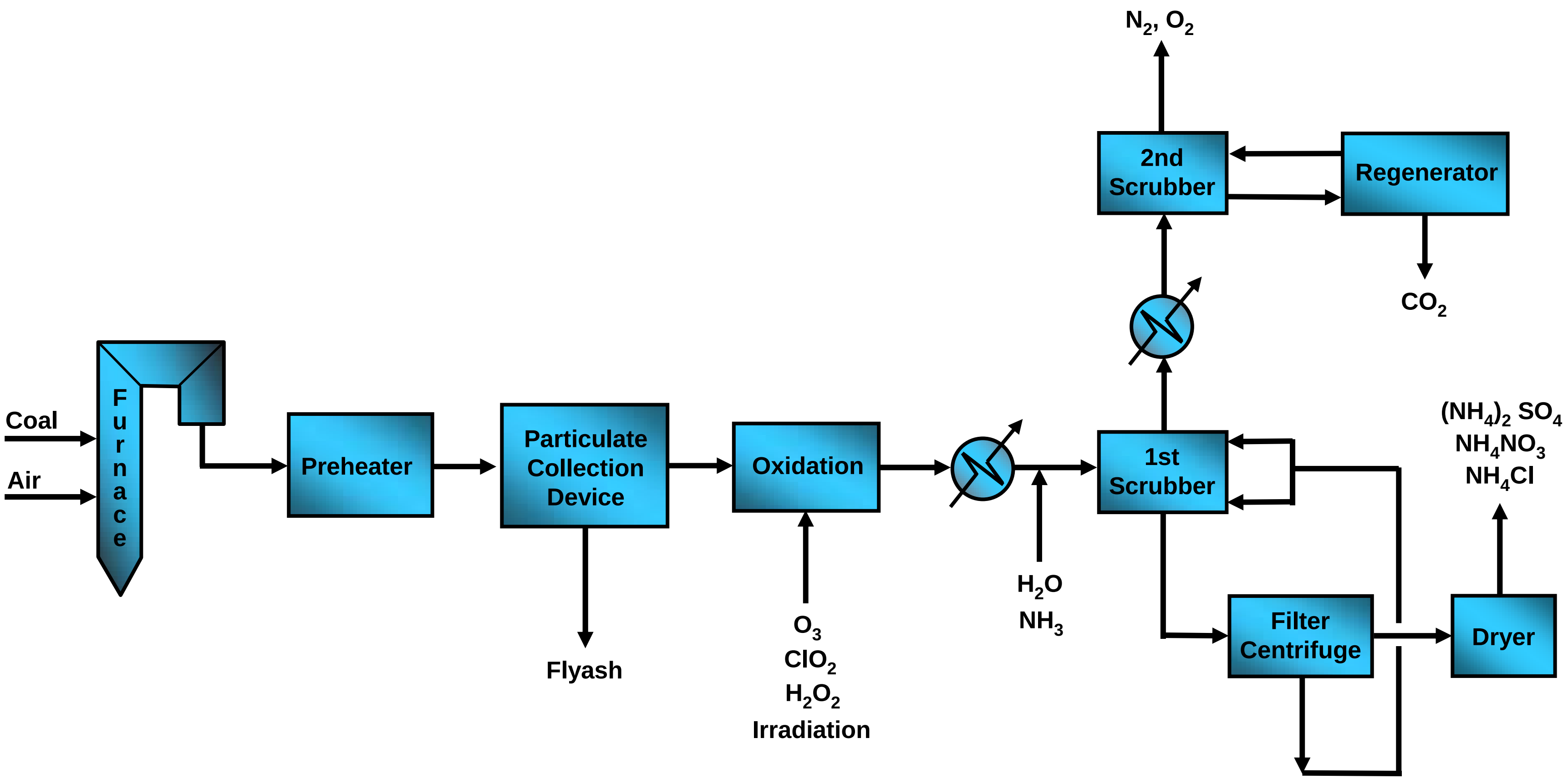
AQUA AMMONIA PROCESS CHEMISTRY
(regeneration)

- $2\ NH_4HCO_3(aq) \longrightarrow (NH_4)_2CO_3(aq) + CO_2(g) + H_2O$
- $NH_4HCO_3(aq) \longrightarrow NH_3(aq) + CO_2(g) + H_2O$
- $(NH_4)_2CO_3(aq) \longrightarrow 2\ NH_3(aq) + CO_2(g) + H_2O$

Aqua Ammonia Process



ADVANTAGES OF PROCESS

- Multi-component control of acid gases produced during coal combustion.
- Novel combination of oxidation step with ammonia wet scrubbing.
- Process is regenerable with respect to CO_2 scrubbing.
- Fabrication of a saleable commodity (fertilizer) out of waste materials (acid gases). Serendipitous to the process, the fertilizer may have an impact on terrestrial sequestration.
- Production of a pure CO_2 stream that can further be processed or sequestered.
- Can meet zero pollutant emissions.

ADVANTAGES OF PROCESS

- **As compared to MEA scrubbing, the ammonia process :**
  - has a higher loading capacity
  - will not degrade in the presence of other flue gas components
  - has a lower parasitic power loss
  - will not corrode equipment

Regeneration Heat Requirements for a 14% Aqueous Ammonia Solution Compared to Current MEA Technology					
Process	ΔH_{rx} (kcal/mol)	Sensible Heat (kcal/mol)	Heat of vaporization (kcal/mol)	Total (kcal/mol)	% Reduction from MEA process
MEA	20.0	79.4	18.9	118.3	0
ABC → AC	6.4	36.0	0	42.4	64
ABC → NH_3	24.1	36.0	0	60.1	49
AC → NH_3	15.3	36.0	0	51.3	57

TECHNICAL CHALLENGE

- There is a paucity of experimentally produced data for low temperature aqueous ammonia scrubbing of CO_2 from flue gas. Regeneration information is non-existent.

- Influence of SO_2 and NO_2 components on the ammonia/CO_2 scrubbing is unknown

- The impact of the experimental information on the proposed multi-component control process needs to be defined.

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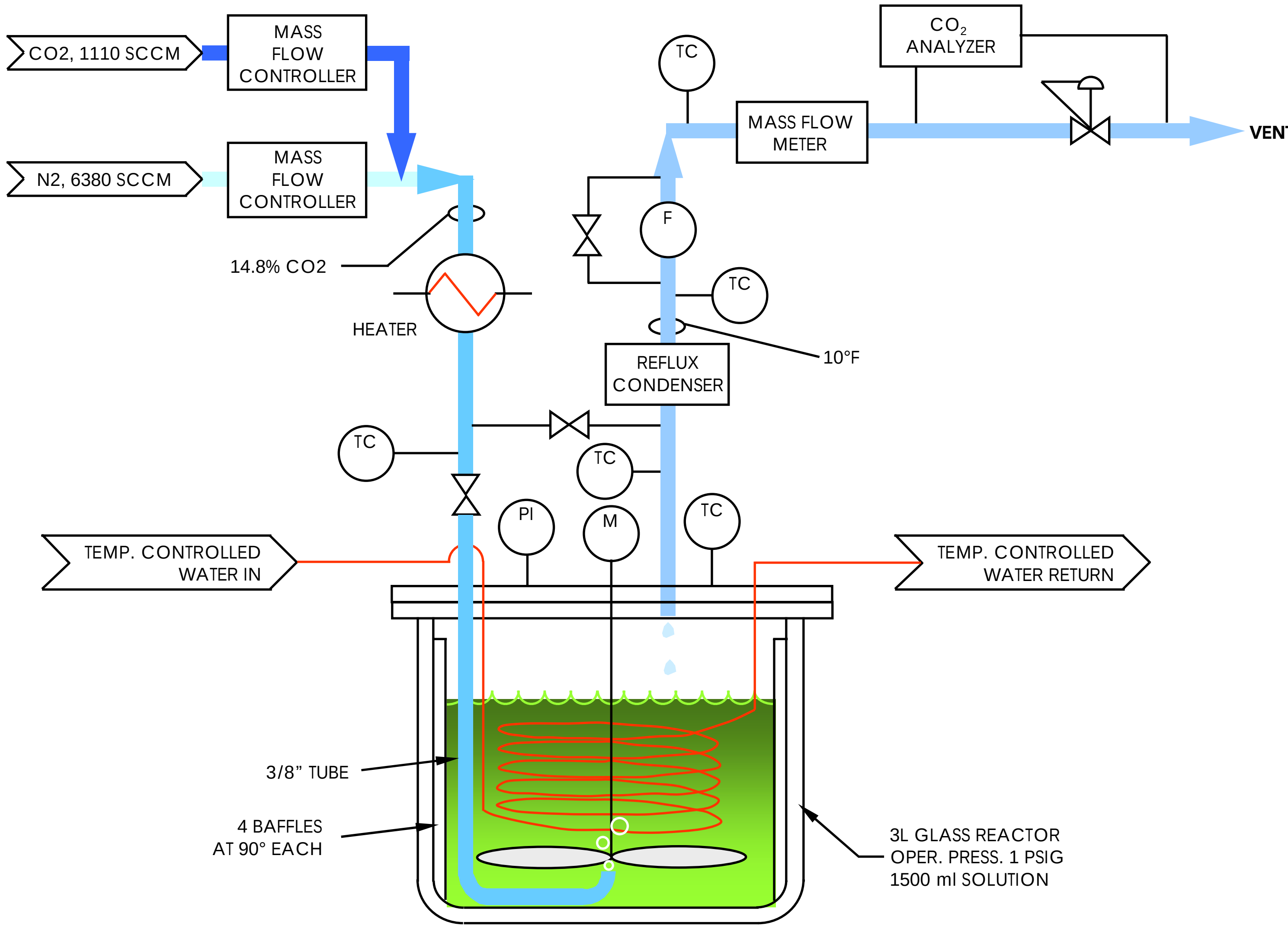
TECHNICAL APPROACH

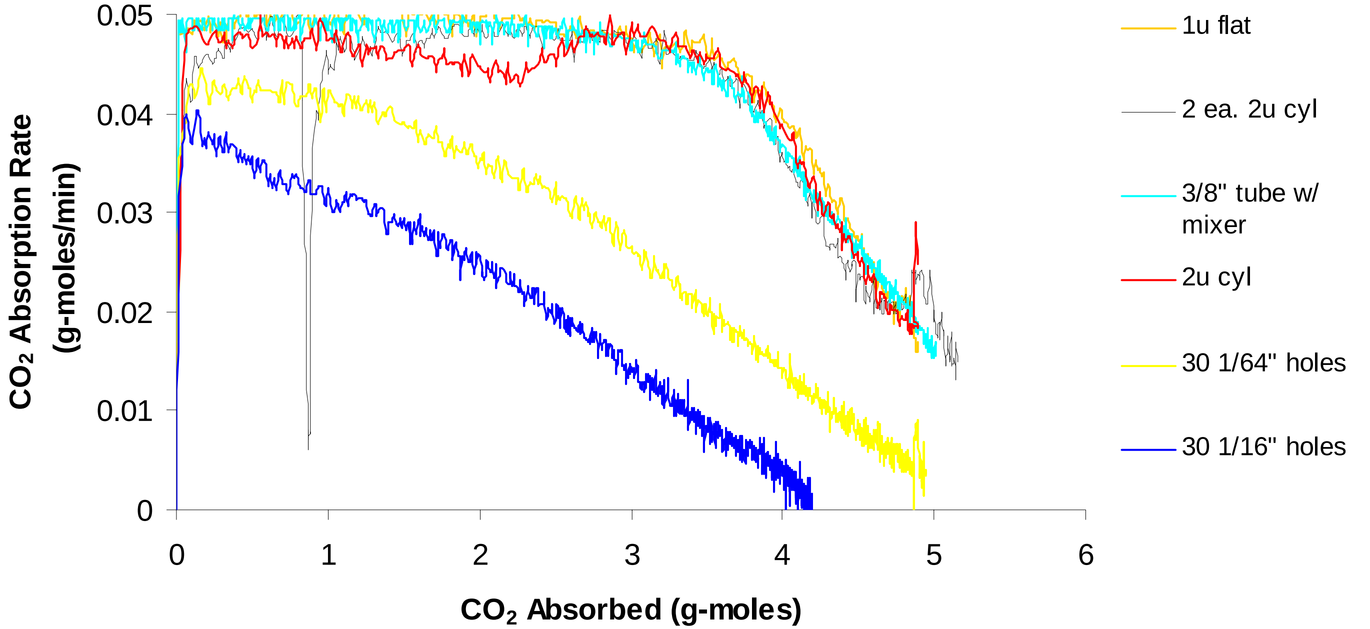
- **Parametric study in a semi-batch reactor system.**
  - Absorption
    - Temperature
    - Ammonia concentration
    - CO_2, NO_x, SO_2 by themselves and collectively
  - Regeneration

- **Incorporate information into a mathematical model to be used for sensitivity studies and eventual scale-up of system.**


CO2, 1110 SCCM
MASS FLOW CONTROLLER
N2, 6380 SCCM
MASS FLOW CONTROLLER
14.8% CO2
HEATER
TC
TC
MASS FLOW METER
CO_2 ANALYZER
VENT
F
TC
10°F
REFLUX CONDENSER
TC
PI
M
TC
TC
TEMP. CONTROLLED WATER IN
TEMP. CONTROLLED WATER RETURN
3/8" TUBE
4 BAFFLES AT 90° EACH
3L GLASS REACTOR
OPER. PRESS. 1 PSIG
1500 ml SOLUTION

PARAMETRIC SCAN IN REACTOR SYSTEM

- Ammonia concentration: 7, 14, 21 wt%
- Temperature: 60, 80, 100 ºF
- Reactor/solution volume: 3.0/1.5 liter
- Gas flow: 7500 sccm
- CO_2 concentration: 15 vol%
- Pressure: ambient

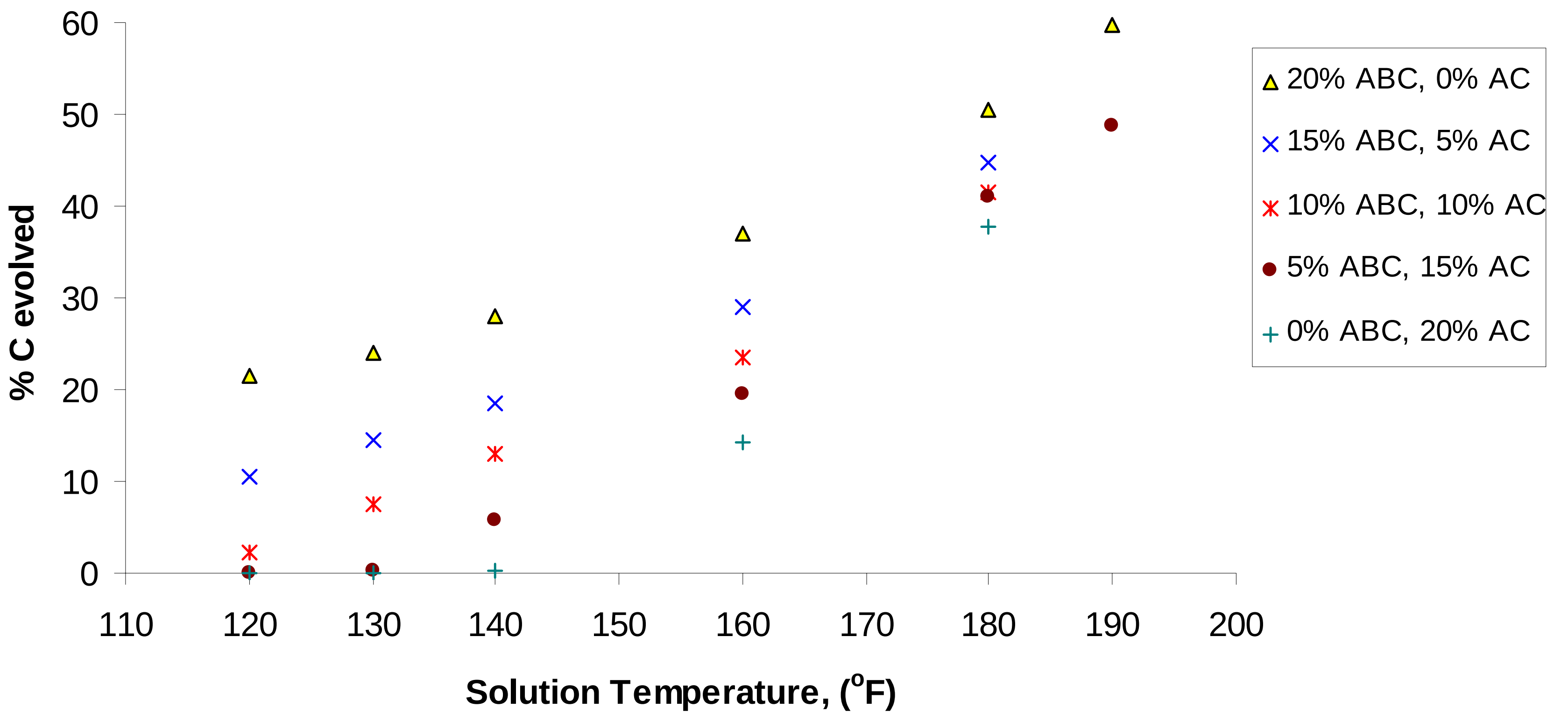


Effect of Sparger Types (CO_2 absorbed)

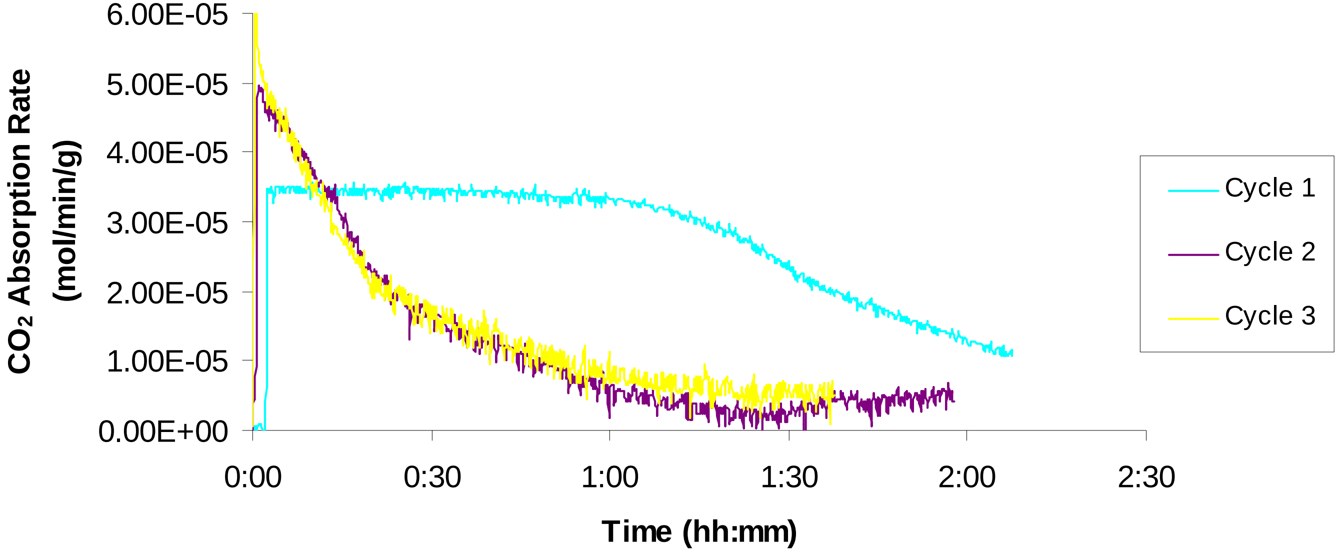
IMPACT OF TEMPERATURE

Temperature, °F	*Initial Rate, mole-CO_2 /min*	*Initial Conversion, mole %*	*CO_2 Loading, kg-CO_2/kg NH_3*
60	0.040	80.1	1.2
80	.048	96.1	1.1
100	.043	86.1	1.0

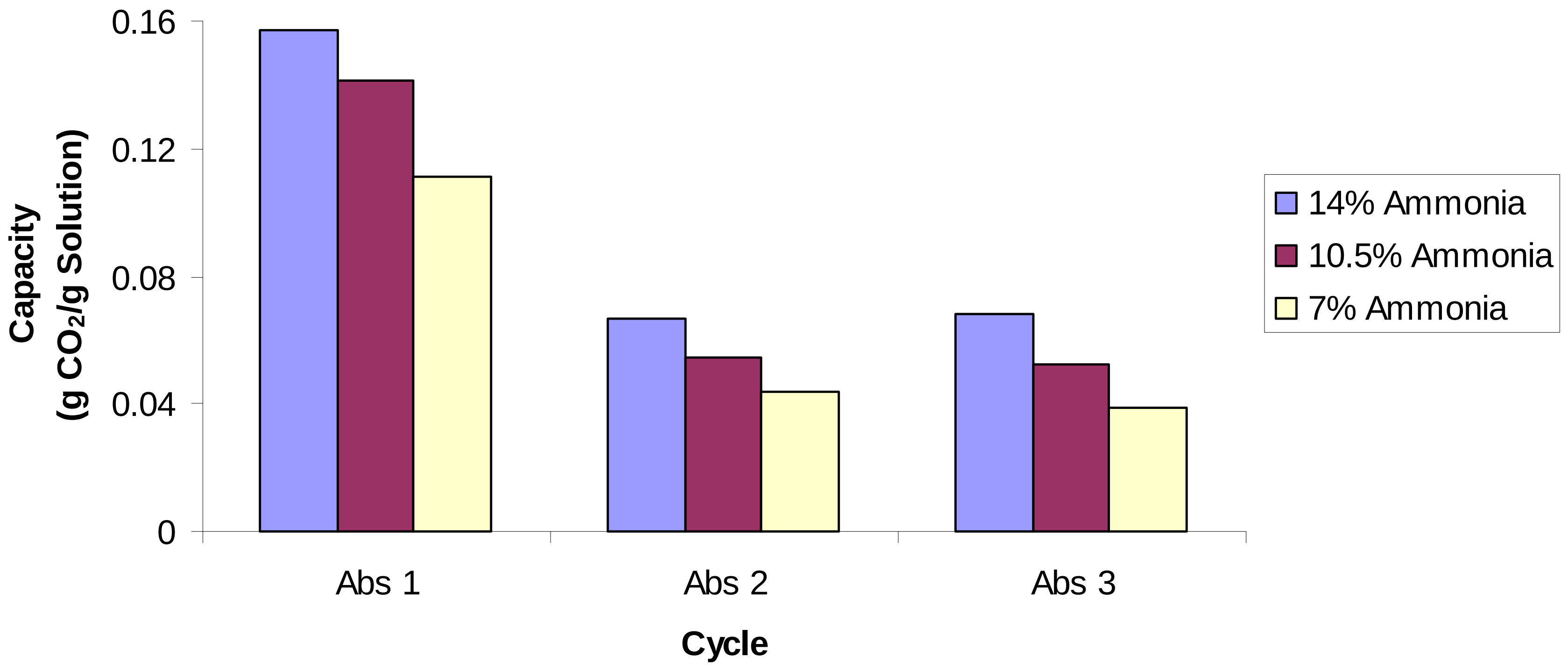
14% Ammonia Concentration



Regeneration Test Summary



CO_2 Absorption Rate with 14% NH_3 Solution



Effect of Cycling on CO_2 Absorption Capacity

SUMMARY

- Reaction rate information obtained on 7 %, 14%, and 21% ammonia solutions at 60°F, 80°F, and 100°F.
- Thermal regeneration of ammonium bicarbonate and ammonium carbonate solutions demonstrated ability to release up to 60% of carbon in solutions.
- Regeneration energy reductions of >60% over current MEA technology were determined.
- Cycling tests determined the effective loading capacities of ammonia solutions after three absorption/regeneration cycles.